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HYBRID FILM PROPERTIES OF THE LINSEED OIL BASED ALKYD RESIN MODIFIED WITH GLYCIDYL POLYHEDRAL OLIGOMERIC SILSESQUIOXANE

M.Sc. THESIS

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GLİSİDİL POLİHEDRAL OLİGOMERİK SİLSESKUOKZAN KATKILI KETEN YAĞI ESASLI ALKİD REÇİNELERİN HİBRİT FİLM ÖZELLİKLERİ

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Sibel SOGUKKANLI, a **M.Sc.** student of ITU **Graduate School of Science Engineering and Technology** student ID 506111022, successfully defended the **thesis** entitled "**HYBRID FILM PROPERTIES OF THE LINSEED OIL BASED ALKYD RESIN MODIFIED WITH GLYCIDYL POLYHEDRAL OLIGOMERIC SILSESQUIOXANE**", which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

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To my dearest family,

FOREWORD

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ABBREVIATIONS

POSS **:** Polyhedral Oligomeric Silsesquioxane
GPOSS **:** Glycidyl Polyhedral Oligomeric Silsesquioxane
FT-IR **:** Fourier Transform Infrared Spectrophotometer
^{1}H-NMR **:** Nuclear Magnetic Resonance Spectroscopy
DSC **:** Differential Scanning Calorimeter
TGA **:** Thermogravimetric Analysis
SEM **:** Scanning Electron Microscopy
PG **:** Partial Glyceride
PA **:** Phthalic Anhydride
1MI **:** 1-Methylimidazole
LA-GPOSS **:** Linseed Oil Modified Alkyd Resin with GPOSS
$CDCl_3$: Deuterium Chloroform

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HYBRID FILM PROPERTIES OF THE LINSEED OIL BASED ALKYD RESIN MODIFIED WITH GLYCIDYL POLYHEDRAL OLIGOMERIC SILSESQUIOXANE

SUMMARY

Hybrid materials can be defined as materials made of two different moieties such as organic and inorganic components combined on the molecular scale. Numerous hybrid organic–inorganic materials have been developed, providing access to an immense new area in materials science. The development of these multi-functional advanced materials has a major impact on future applications in protective coating fields due to consisting of a combination of organic polymers' advantages such as lightweight, flexibility, good impact resistance and good process ability and inorganic materials' advantages such as good chemical resistance and high thermal stability.

Alkyd resins are essentially polyesters made by heating polyhydric alcohols with polybasic acids or their anhydrides and used mostly in making protective coatings with good corrosion properties. These resins are useful as film forming component in paint, varnished, coatings. Hence, alkyd resins are one of the significant elements in the synthetic paint industry. Despite the growing popularity of acrylic, polyurethane and epoxy resins, alkyd resins remain highly favoured among paint producers due to its variability of compositions and better value for money. Originally, alkyd resins are the reaction products of phthalic anhydride and glycerol. But these products were too brittle to make satisfactory coatings. The use of oils or unsaturated fatty acids in the formulation yields the air-drying coatings which enhanced the features of alkyd resins in the coating industry. Alkyd resins products are suitable for wide range of products with application in decorative and maintenance paints where excellent gloss and good durability are required. Recently, alkyd resins were modified with inorganic materials to improve their processing, thermal and mechanical properties for using as coating materials.

The recent development of hybrid materials and polymerizable macromers based on polyhedral oligomeric silsesquioxanes (POSS) afford a tremendous opportunity for preparation of new thermoset material formulations. POSS systems containing polymerizable reagents have two primary aspects. Conserning this, their composition is truly hybrid, containing an inorganic framework which is externally covered (and solubilized) by organic substituents. These POSS reagents have a number of desirable physical properties as well. For example, they are highly soluble in common organic solvents such as tetrahydrofuran, toluene, chloroform and hexane. They have high thermal stabilities, and can be polymerized using standard polymerization method (i.e. radical, condensation, ring opening polymerizations etc.) to provide polymers with a variety of architectures. These two features and the fact that such systems are readily copolymerized with most wholly organic polymers provide the materials introducing and manipulating many properties to polymer systems.

By considering above mentioned advantages of hybrid reagents, in the present study, glycidyl polyhedral oligomeric silsesquioxane (GPOSS) was used as inorganic particule to combine with linseed oil together with phthalic anhydride (PA) as a new material for oil based binder. For this aim, partial glyceride (PG) mixture was firstly synthesized by the glycerolysis reaction. Then, hydroxyl groups of PG attack the anhydride molecules forming a monoester with a carboxyl group. The monoesters then react with the epoxides of GPOSS to form diester and a new secondary hydroxyl group. In this reaction, 1-methylimidazole (1MI) was used as catalyst Inorganic content of the mixture was adjusted to 2-10 wt % based on PG content. Above 5 wt% amount of GPOSS however, roughness sets on film surface because in the present of excess GPOSS forms high crosslinking which leads to insoluble inorganic domains in the polymer matrix. The mixture of reactants was homogenized with mechanical stirrer at room temperature for 1 hour. Then, the temperature was rised to 200 ^{o}C and maintained at this temperature for 2 hours. Thus, the GPOSS modified alkyd resin (LA-GPOSS) was subjected to structural and thermal analysis.

The formation of chemical bonding between GPOSS and alkyd resin was examined by FT-IR and ^{1}H-NMR. These results confirmed that GPOSS molecules were chemically incorparated to the linseed oil alkyd resins through both ring opening reaction of epoxide/anhydride and esterification reaction of hydroxyl/anhydride. Furthermore, DSC analysis showed that the epoxide groups take part into the reaction at 200 ^{o}C, which is consistent with the applied temperature in the synthesis step. The exotherm temperature for LA-GPOSS were found to be lower than that of neat alkyd resin due to the catalytic affect of 1MI used in the LA-GPOSS. Thermal stability of the hybrid materials was investigated by TGA under nitrogen atmosphere. Thermal stability was increased by increasing GPOSS amount.

In the end, the film properties of obtained LA-GPOSS samples were determined according to the related ASTM standarts. The obtained samples showed good film properties such as drying, flexibility, adhesion, and water, alkali and acid resistances. The best film properties of obtained sample was with 5% wt of GPOSS.

GLİSİDİL POLİHEDRAL OLİGOMERİK SİLSESKUOKZAN KATKILI KETEN YAĞI ESASLI ALKİD REÇİNELERİN HİBRİT FİLM ÖZELLİLERİ

ÖZET

İki ya da daha fazla malzemenin, daha üstün termal, mekanik özellikler göstermesi için mikro/makro seviyede heterojen karışımlarını oluşturarak elde edilen malzemelere hibrit malzemeler denir. Fonksiyonel malzemeler, organik polimerlerin hafiflik, esneklik, darbe direnci ve kolay işlenebilirlik gibi özellikleri ile inorganik maddelerin kimyasallara karşı direnç, yüksek sıcaklık dayanımı, kırılganlık gibi avantajlarını brilikte içermektedirler.

Alkid reçineler, başta kaplama ve boya endüstrisi olmak üzere bir çok kullanım alanına sahip, yaygın ve çeşitli kapasitelerde üretimi yapılabilen ürünlerdir. Aynı zamanda alkid reçineler, poliasit ve poliollerin kondenzasyon sonucu oluşan polyesterlerdir. Bu reaksiyonlar sonucunda ise düz zincirli alkidler elde edilir. Bu şekilde elde edilen alkid reçinelerin kullanım alanları sınırlı olduğundan, diğer reçinelerle, yağlarla veya daha basit yapıdaki alkol ve asitlerle modifiye edilmektedirler. Kullanılan maddelerin özelliklerine göre; hızlı kuruyan, sert ve düşük esneklikli film özelliklerinden yavaş kuruyan, yumuşak ve esnek film özellikli alkid reçinelere kadar geniş çalışma alanına hitap eden kaplama malzemeleri elde edilebilir. Alkid reçinelerin ticari üretimlerinde yağ ya da yağ asidi kullanımı içerikli iki farklı metot vardır. Yağ asidiyle yapılan reçinelerde; doymamış yağ asidi, poliol ve asit anhidrit; ürün istenen viskoziteye ulaşana kadar kürlenir. Yağ kullanılan reçinelerde ise, önce trigliseritler poliol ile birlikte gliseoliz reaksiyonu sonucu monogliserit hale getirilir. Daha sonra, bu karışıma asit anhidrit ilave edilerek esterifikasyon reaksiyonu yardımıyla alkid reçine elde edilir. Her iki alkid reçine üretim yönteminde de, reçine çeşitli filtreleme yöntemleriyle saflaştırılır ve boya ve vernik üreticilerinin kullanımına hazırlanmak üzere seyreltilir.

Alkid reçineler diğer reçinelere göre uygulama süresi boyunca film tabakası halinde kalabilen düşük maliyetli kaplama malzemeleri oluşturabilmektedirler. Fakat, alkid film kaplamaların çevresel şartlara olan dayanımları akrilik ve poliüretan'dan elde edilen film tabakalarınınkine göre daha düşüktür. Ayrıca alkid reçinelerin polyester zincir içeriklerinden dolayı ester grupları kolaylıkla hidroliz olabilmektedir. Bundan dolayı alkid reçinelerinden elde edilen filmler, suya, alkalilere ve asitlere karşı hassastırlar. Fakat tüm bu dezavantajlara karşın istenilen performansa ulaşabilmek için alkid reçineler birden fazla fonksiyonel grupla modifiye edilebilmektedirler. Diğer taraftan, alkid reçinelerin ester yapıları aynı yağ uzunluğuna sahip epoksi esterlere göre ultraviyole ışınlara ve ısıya karşı dayanıklı olup, parlaklık ve renkliliklerini uzun süre koruyabilmektedirler.

Polihedral oligomerik silseskuoksan (POSS) molekülleri monomerik ve polimerik yapıların güçlendirilmesi için kullanılan son zamanarda oldukça popüler olan kimyasal malzemelerdir. POSS katkılı polimerlerin termal ve mekanik özelliklerindeki iyileşme birçok bilim adamının dikkatini çekmiştir. POSS

molekülleri üç boyutuda nanometre seviyesinde olan kübik şekilli dolgu malzemeleridir. POSS molekülleri bir yada daha fazla fonksiyonel organik gruplar içerebilmektedirler. Bu nedenle bilinen polimerlere kopolimerizasyon, aşılama yoluyla veya fiziksel karışım yollarıyla POSS molekülleri katkılanmaktadırlar. POSS molekülleriyle güçlendirilmiş nanokompozitler ile ısıl dayanımları artmış yüksek sıcaklıklarda kullanılabilen, oksidasyona karşı kararlı, mekanik özellikleri yüksek, alev alma özelliği düşük, açığa çıkan ısı miktarı az ve işlem viskoziteleri düşük olan malzemeler üretilebilmiştir. POSS molekülleri basamaklı, kafes ve kısmi kafes yapılar gösterebilmektedirler. POSS molekülleri, silisyum/oksijen atomlarından oluşan kafes (anorganik kısım) yapısı ve bu silisyum atomuna bağlı fonksiyonel hidrokarbon gruplarından (organik kısım) oluşan hibrit malzemelerdir.

POSS monomerleri diğer monomerler içerisinde çözülerek kopolimerizasyon reaksiyonları için kolay reaksiyona girebilme yeteneği kazanabilirler. Monomer fonksiyonlu POSS molekülleri ise tek başlarına dahi polimer eldesinde kullanılabilmektedirler. Polimerleşme işleminde, POSS molekülleri reaksiyon karışımının entropisini düşürerek reaksiyon sırasında faz ayrımına veya polimerik yapıya ulaşmadan faz olarak ayırılmaya neden olabilirler. POSS molekülü katkılı polimerik malzemeleri özellik bakımından polimer ve seramik bölge arasında yer almaktadırlar. POSS yapılar iki önemli özelliğe sahiptirler. İlki, hibrit kimyasal bileşiminliolmalarıyla silika ve silikon malzemeler arasında bir özellik göstermeleridir. İkincisi ise, POSS moleküllerinin 1-3 nm arasında değişen büyüklüklere sahip olmalarıdır. Bu büyüklükteki POSS molekülleri moleküler boyuttaki polimerik zincirler arasına çok rahat bir şekilde girebilmekte, böylece polimer matrisini güçlendirmektedirler. Ancak, her POSS molekülü yüzeyinde silika, silikon ve dolgu maddelerinden farklı olarak bir de organik grup içermektedir, bu durum POSS nano yapılarının polimer, biyolojik sistemler, veya yüzeylerle uyum içerisinde olmasına yardımcı olmaktadır. POSS ile modifiye edilen polimerik malzemelerin yüksek sıcaklıkta kullanılabilirlikleri, oksidasyon dirençleri ve mekanik, yanmazlık, viskozite gibi özelliklerinde gelişmeler gözlenmiştir.

Bu tezde, klasik alkid reçine bileşenleri olan, kısmi gliserit ve fitalik anhidrit'e farklı besleme oranlarında glisidil POSS (GPOSS) nanomalzemesi ilave edilerek yeni hibrit malzemeler sentezlenmiştir. Bu amaçla ilk önce keten yağı ve gliserolün gliseroliz reaksiyonuyla kısmi gliserit (PG) karışımı elde edilmiştir. PG'in hidroksil grupları anhidrit molekülüne saldırarak halka açılması sonucu monoester bileşiklerini oluştururlar. Elde edilen monoesterler GPOSS'un epoksit gruplarıyla reaksiyona girerek ya ikincil alkol içeren diester moleküllerinin oluşmasını yada epoksit halkalarının protanlanarak halka açılmasını sağlarlar. Halka açılması aktif uç grup yada aktiflenmiş monomer mekanizmaları üzerinden yürüyen bir polieterleşme reaksiyonudur. Epoksitlerin zincirlerle çapraz bağlanma miktarlarını arttırmak ve reaksiyonu hızlandırmak için katalizör olarak 1-metilimidazol kullanılmıştır. Karışımın inorganik içeriği GPOSS' un çözünürlüğü göz önüne alınarak ağırlıkça 2-10% olarak ayarlanmıştır. Reaksiyon karışımın ilk olarak 1 saat mekanik karıştıcı ile homojenize edilip ardından 2 saat boyunca 200 ^{o}C'de kürlenmesiyle gerçekleştirilmiştir.

Alkid reçine ve GPOSS arasındaki kimyasal bağ yapılarının analizleri FT-IR ve ^{1}H-NMR cihazlarıyla gerçekleştirildi. Her iki yöntemde elde edilen sonuçlardan, GPOSS molekülleri üzerindeki epoksit halkalarının açılarak alkid reçineye bağlandığı gözlemlenmiştir. Buna ek olarak, numunelerin termal özellikleri TGA ve DSC analizleriyle belirlenmiştir. Elde edilen hibrit malzemeler saf alkit reçinelere göre,

daha yüksek sıcaklıklarda bozunmakta ve daha gelişmiş ısıl kararlılık göstermektedirler. Termal özelliklerdeki bu dikkat çekici artış, yüksek çapraz bağ yoğunluğu ve POSS moleküllerinin üç boyutlu ağ yapısından kaynaklanmaktadır.

Ayrıca elde edilen hibrit malzemelerinin film özellikleri ASTM standartlarına uygun şekilde esneklik, yapışma, sertlik, su, asit ve baza dayanıklılık testleri ile incelenmiştir. %5 üzerinde besleme oranlarına sahip örneklerdeki çapraz bağ yoğunluğunun fazla olması sebebiyle bu malzemeler film özelliklerini kaybetmiştirler. Bu şartlarda gerçekleştirilmiş reaksiyonlar içerisinde %5' e kadar GPOSS yapısı içeren hibrit malzemelerin yapılan analizler sonucunda en iyi özellikleri gösterdiği tespit edilmiştir.

1. INTRODUCTION

Hybrid materials based on incorporation of nano-sized inorganic particles into polymer matrices have gained considerable attention due to consisting of a combination of organic polymers' advantages such as lightweight, flexibility, good impact resistance and good process ability and inorganic materials' advantages such as good chemical resistance and high thermal stability. Principally, two different approaches can be used for the formation of hybrid materials i) well-defined preformed building blocks are reacted with each other to form the final hybrid material in which the precursors still at least partially keep their original integrity and ii) one or both structural units are formed from the precursors that are transformed into a novel network structure[1].

Alkyd resins are the polymeric esters which are obtained by esterification of polyols with polycarboxylic acids. The resins prepared in this way are brittle and can not be employed as a coating material. Due to this fact, oils were used to modify the alkyd resins[2, 3]. Since long chains of the fatty acids incorporated into the resin matrix, the brittleness is prevented and the film becomes flexible. The vegetable oils are very versatile materials for oil based binder production. Besides giving flexibility, they provide additional crosslink through oxidative polymerization. In the coating industry, the most commonly used oil-modified alkyd resins contain drying or semidrying oils, mostly linseed oil, for enhancement of the drying characteristics of films[4]. For production of oil modified alkyd resins, there are two specific methods which are called monoglyceride (glycerolysis) and fatty acid processes. Triglycerides are converted to a mixture of monoglycerides and diglycerides in the glycerolysis process whereas free fatty acids obtained by spliting triglyceride are used instead of some part of polybasic acids in the fatty acid process[5]. Therefore, alkyd resins which can be produced from renewable natural resources are used as an organic component of hybrid materials.

Polyhedral oligomeric silsesquioxane (POSS), which was used as an inorganic particle for hybrid materials have drawed much attention recently due to the

nanometer size, facility of which these particles can be integrated into polymeric materials and the uncommon effectiveness to bolster polymers[6-10]. Incorporation of functional POSS into thermosetting polymers often exhibits dramatic improvements such as high glass transition temperature, excellent oxidation resistance and high mechanical strength in performance[11, 12]. There are a few reports for the synthesis of hybrid materials from vegetable oil-based resin and multi-functional POSS structures.

In continuation to these studies, the present study is based on using the glycidyl POSS (GPOSS) for the modification of oil-based alkyd resin. For this aim, typical simple linseed oil modified alkyd resin was synthesized by the addition of GPOSS in accordance with the formulation and procedure of literature[13]. In the reaction, epoxides of GPOSS molecules were linked to hydroxyl group of modified linseed oil by means of monocarboxylic ester of phthalic anhydride. It was found that the curing reaction should be conducted in basic media to favour polyesterification mechanism. The addition of 1-methylimidazole as a base catalyst not only promoted the polyesterification reactions but also prevented undesirable polyetherification reactions. Since, they result in unreacted anhydrides or acid monoesters in the resin[14-16].

The ratio of glycidyl POSS nanoparticles on the properties of the hybrid films, such as thermal and morphological properties have been systematically investigated using techniques including FT-IR, ^{1}H-NMR, DSC and TGA. Film properties such as flexibility[17], adhesion[18], water resistance[19], alkali resistance[19] acid resistance [19] and drying time[20] were also determined according to ASTM.

2. THEORETICAL PART

2.1 Composition and Chemistry of Vegetable Oils

Vegetable oils are composed of triglycerides extracted from seeds of plant[1]. Triglycerides consist of adding three molecules of fatty acids to a glycerol molecule as shown in Figure 2.1[21].

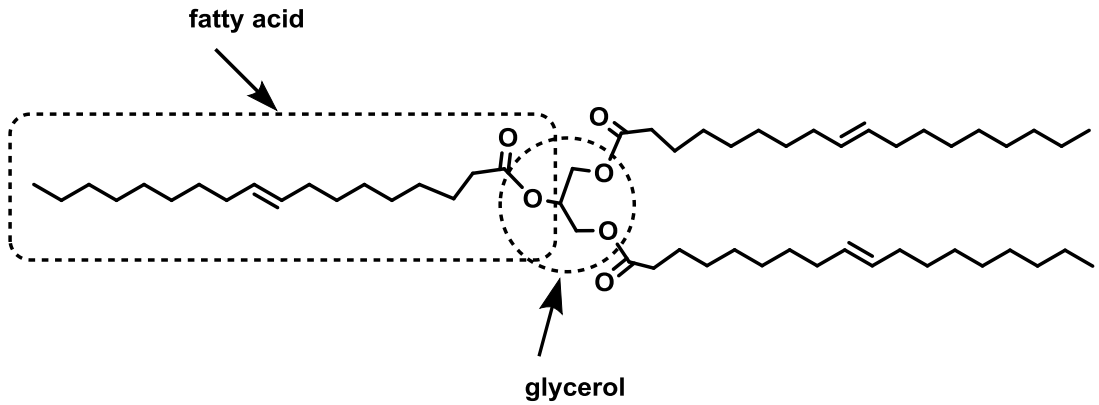

Figure 2.1 : Triglyceride molecule, the major component of vegetable oils

The most efficient parameters for the physical and chemical properties of vegetable oils are the stereochemistry of the double bonds, the degree of unsaturation and the length of the carbon chain of the fatty acids[22, 23]. The degree of unsaturation can be asserted by the iodine value (IV) (amount of iodine in g that can react with double bonds present in 100 g of sample under specified conditions), which can be used as a key parameter to divide oils into three classes: drying (IV: 170, linseed oil), semi-drying (IV: 100- 170, sunflower) and non-drying (IV: 100, palm kernel oil) oils[21]. The iodine values and fatty acid compositions of common vegetable oils are summarized in Table 2.1.

Table 2.1 : Properties and fatty acid compositions of the most common vegetable oils.

Vegetable oil	Double bonds[a]	Iodine value[b] (mg/100g)	Fatty acids (%)				
			Palmitic	Stearic	Oleic	Linoleic	Linolenic
Palm	1.7	44-58	42.8	4.2	40.5	10.1	–
Olive	2.8	75-94	13.7	2.5	71.1	10.0	0.6
Groundnut	3.4	80-106	11.4	2.4	48.3	31.9	–
Rapeseed	3.8	94-120	4.0	2.0	56.0	26.0	10.0
Sesame	3.9	103-116	9.0	6.0	41.0	43.0	1.0
Cottonseed	3.9	90-119	21.6	2.6	18.6	54.4	0.7
Corn	4.5	102-130	10.9	2.0	25.4	59.6	1.2
Soybean	4.6	117-143	11.0	4.0	23.4	53.3	7.8
Sunflower	4.7	110-143	5.2	2.7	37.2	53.8	1.0
Linseed	6.6	168-204	5.5	3.5	19.1	15.3	56.6

[a)] Average number of double bonds per triglyceride.
[b)] The amount of iodine (mg) that reacts with the double bonds in 100g of vegetable oil.

2.2 Vegetable Oil-Based Polymers

Polymers are largely the most essential products of the chemical industry that are used in various applications in daily life. Fossil materials are the main sources for almost all polymers[5]. However, natural products for industrial applications are becoming very important due to carrying social, environmental and energy advantages when they compared with non-renewable resources whose reduction and waste disposal issues are huge problems for the industries[5, 24-26]. The vegetable-oil-based polymers are biodegradable and cheaper than petroleum-based polymers in many cases. The life cycle of these polymers is shown in Figure 2.2[5].

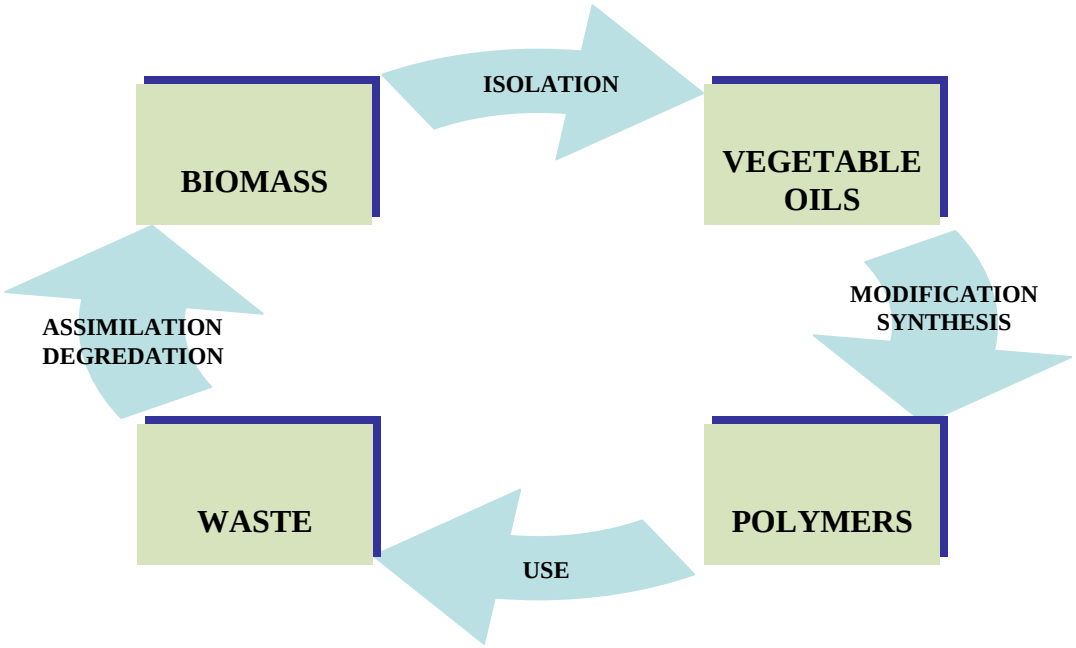

Figure 2.2 : Life cycle of vegetable-oil-based polymers

Triglyceride molecules consist of various reactive positions that are suitable for chemical reactions: ester groups, double bonds, allylic positions and the α-position of ester groups (Figure 2.3). These can be used to polymerize triglycerides with polymerizable groups to obtain thermosets. Therefore, triglycerides can utilize as polymer additives (e.g., epoxidized soybean oil as plasticizer), as building blocks for thermoplastic polymers (e.g., dicarboxylic acids such as azelaic, sebacic, and dimer acid for polyesters or polyamides) or as a basis for thermosets. Additionally, plant oils have been applied for paint formulations, coating and resin applications[27].

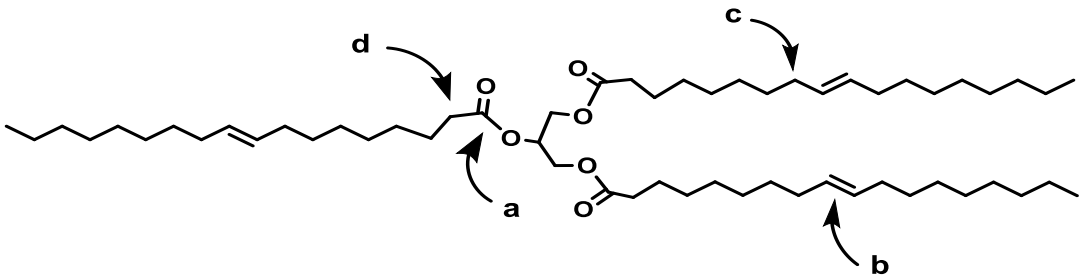

Figure 2.3 : Reactive positions in triglycerides: ester groups (a), double bonds (b), allylic positions (c) and the α-positions of ester groups (d).

2.2.1 Direct polymerization of triglycerides

Triglyceride molecules can be polymerized through a free radical or a cationic mechanism due to their C=C double bond substances[28]. The free-radical polymerization of double bonds has received little consideration since the existence

of chain-transfer processes to the many allylic positions in the molecule. Unsaturated nature of drying oils allows them to react with atmospheric oxygen that leads to the formation of a network (Figure 2.4).

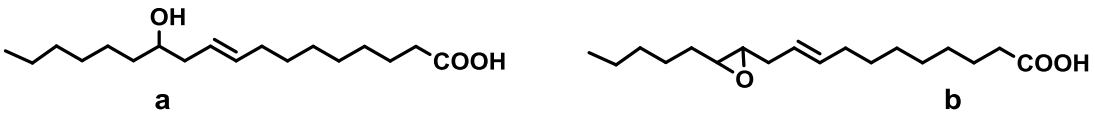

Figure 2.4 : Chemical structures of acids ricinoleic (a) and vernolic (b)

2.2.2 Chemical modification and polymerization of triglycerides

Since the double bonds in the triglyceride molecules are not reactive enough for any potential polymerization, the recently developed modification techniques could facilitate a subsequent polymerization of the triglycerides to produce polymers. There are two main routes for these modifications including epoxidization and glycerolysis reactions.

1. Epoxidization of triglycerides would present epoxide groups, which can be used for condensation and cationic polymerizations (Figure 2.5A).
2. Reduction of the triglycerides to monoglycerides through a glycerolysis reaction provides partial glyceride mixtures, which can be used in condensation reactions (Figure 2.5B)[29].

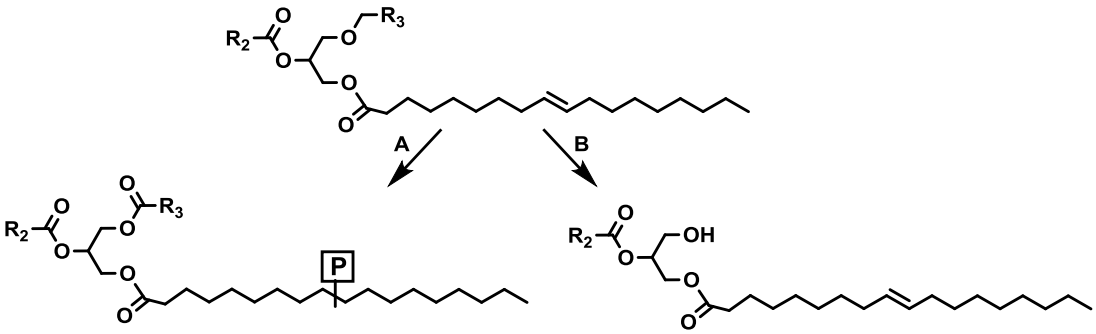

Figure 2.5 : Modification pathways: A) introduction of polymerizable groups into the triglyceride; and B) reduction of the triglycerides to monoglycerides.

2.3 Alkyd Resin

The reaction of triglycerides with glycerol via a glycerolysis generally leads to a mixture of monoglycerides and diglycerides, known as partial glyceride (PG) (Figure 2.6)[29].

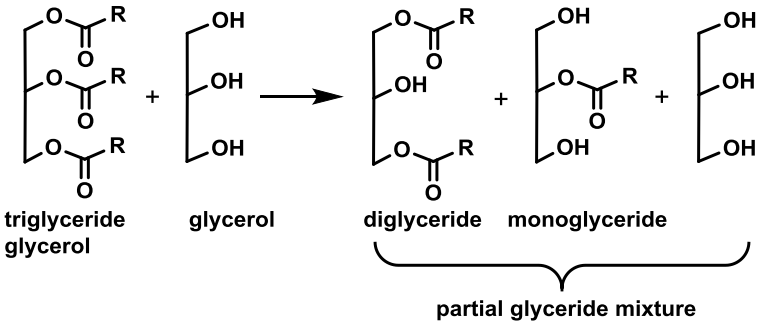

Figure 2.6 : Preparation of partial glycerides

Alkyd resins are one of the oldest polymers from triglyceride oils, and have obtained a good reputation because of their economy and ease of application[30]. Moreover, they are renewable polymers because of oil and glycerol parts[31]. The general procedure for the alkyd resin production is based on polyesterification reaction of anhydrides with polyols, which obtained by the conversion of plant oil triglycerides to monoglycerides (Figure 2.7).

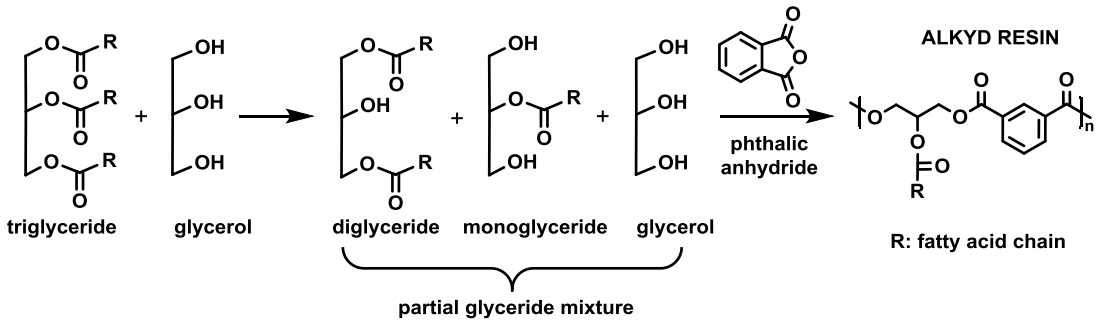

Figure 2.7 : Preparation of alkyd resins

There are two main methods, classical and modified, for the production of alkyd resins. As shown in Figure 2.8, the first step is completely similiar in both methods. In the classical method, calculated amount of glycerol was partially added in the first and second steps and unreacted glycerol was not removed from the reaction medium. In the second method, free glycerol was removed from reaction medium before adding anhydride component[31].

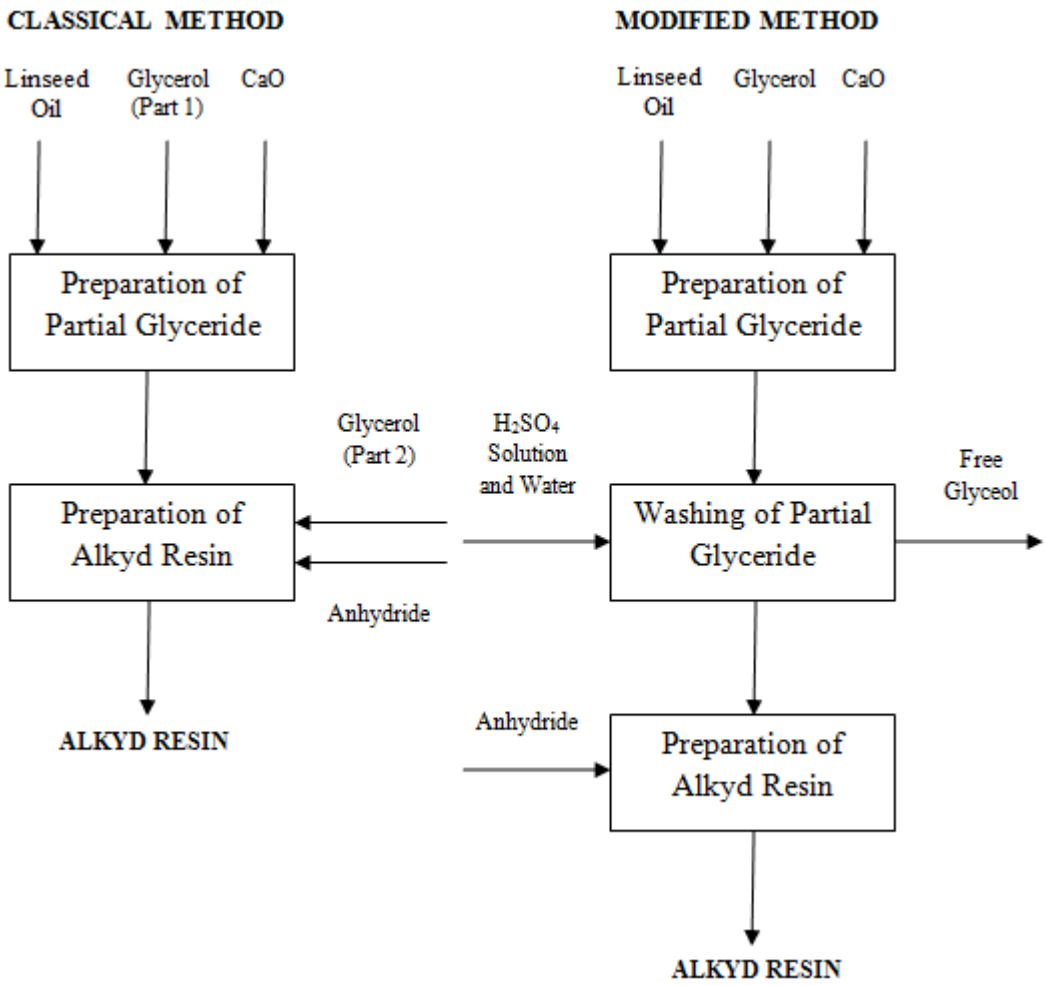

Figure 2.8 : Classical and modified methods for alkyd resin prepration.

2.4 Hybrid Materials

Hybrid materials are used in a extensive scope of application areas such as aerospace, military, construction, electrical and electronics, medicine, marine, transportation etc.[32]. In these applications, the use of polymers often exhibit considerable problems due to low rigidity, low strength and low thermal stability. Therefore, hybrid material technology is developed to satisfy new requirements, such as high use temperatures, high resistance to oxidation, reduced flammability and enhanced mechanical properties[1]. Hybrid materials can be used in many applications of materials chemistry because they are simple to process and are amenable to design on the molecular scale. Commonly these materials are composed of inorganic and organic parts. A more detailed definition distinguishes between the possible interactions connecting the inorganic and organic species. *Class I* hybrid materials are those that show weak interactions between the two phases, such as van

der Waals, hydrogen bonding or weak electrostatic interactions. *Class II* hybrid materials are those that show strong chemical interations between the components. Because of the gradual change in the strength of chemical interactions it becomes clear that there is a steady transition between weak and strong interactions[1]. The dispersed phase component in hybrid materials can be adjusted to molecular levels (a few nanometers) and interfacial interactions between the organic matrix and the nanoparticles which have influence on global properties might provide exponential improvement in material properties. In this respect, inorganic nanoparticles have been incorporated into common polymers to generate a new class of hybrid materials that combine the desirable properties of inorganic nanoparticles (e.g. rigidity, high strength, electrical conductivity, thermal and oxidative stability) with the advantages of polymers (e.g., processability, flexibility, toughness and cost)[33-37].

Nanostructured fillers have dimensions typically ranging from 1 to 100 nm. Based on the nano-scale dimension, they are classified as one-dimensional (clays and graphites)[38-44], two-dimensional (nanofibers, nanotubes or whiskers)[45-47] and three-dimensional (spherical silica, metal particles and semiconductor nanoclusters)[48-55].

2.4.1 Polyhedral oligomeric silsesquioxane (POSS)

Polyhedral oligomeric silsesquioxanes (POSS) which are exceptional examples for three- dimensional nanostructures as displayed in Figure 2.9. In the name of silsesquioxane, the "sesqui" indicates 1.5 oxygens for each silicon $(RSiO_{1.5})_n$, and the suffix "ane" presents a hydrocarbon group, R which could be amine, epoxide, alcohol, carboxylic acid, halide, imide, acrylate, methacrylate, nitrile, vinyl, thiol. Therefore, there are numerous variety of obtained POSS macromonomers with keeping main cage structure[6, 8, 10, 56].

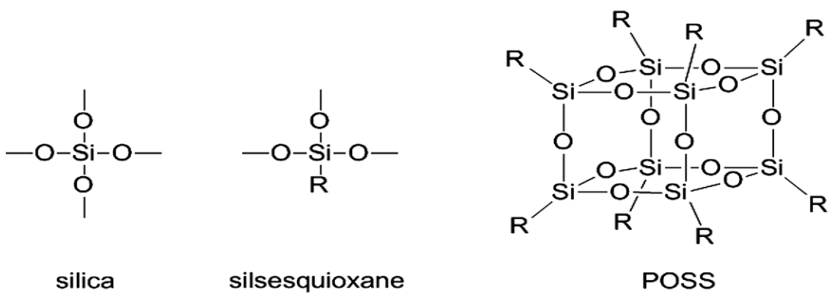

Figure 2.9 : Names and chemical structures of the Si-O bond-containing compounds.

The POSS molecules can be modified by the reactive groups for copolymerization and non reactive groups for enhancing its solubility in organic solvents. Then, these modified POSS macromonomers can give reaction with themselves or other organic monomers by occuring covalent bonds[57-59].

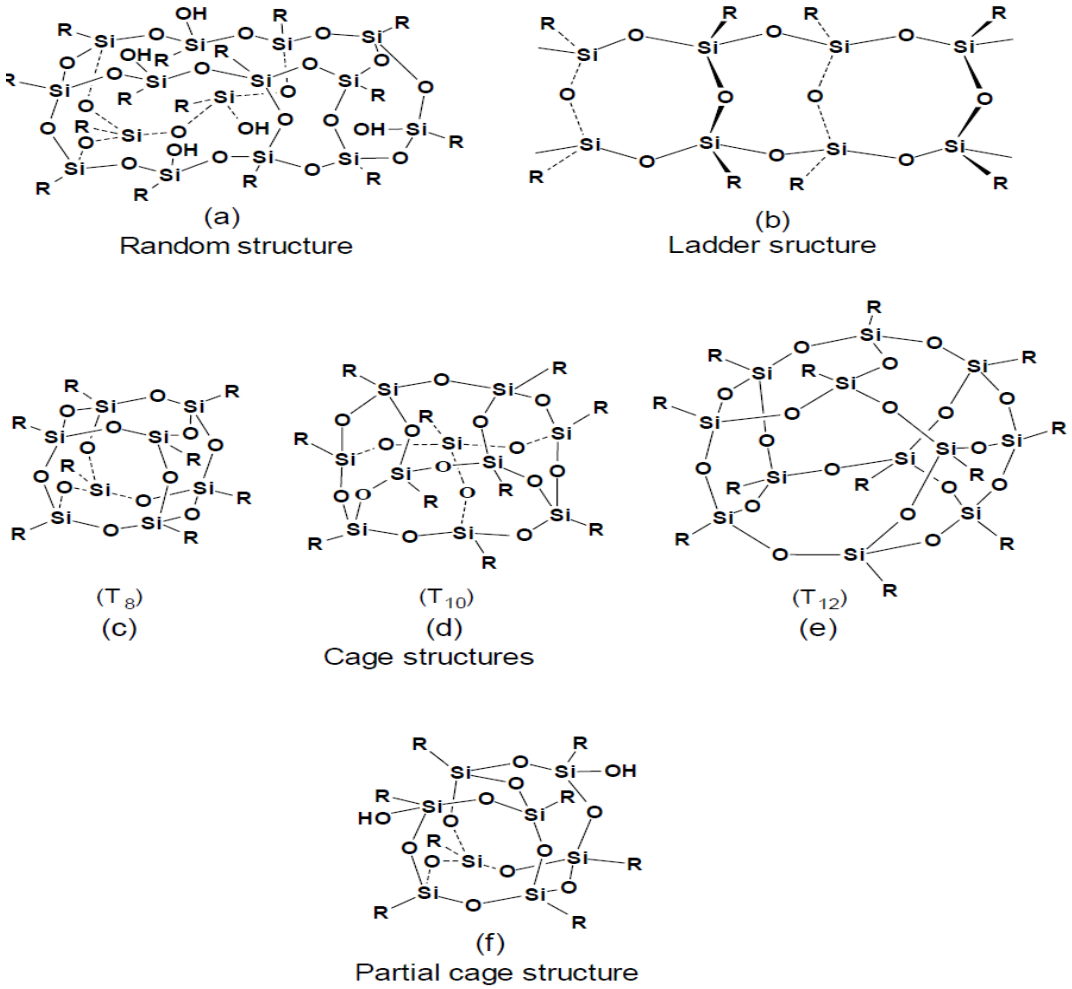

Figure 2.10 : Structure of silsesquioxanes.

As shown in Figure 2.10, different types of silsesquioxanes are commercially available including random, ladder, cage and partial cage structures. Moreover, simple POSS molecules consist of inorganic silicon and oxygen cages, $(SiO_{1.5})_n$ n= 6, 8, 10 or 12, which are respectively cited as T8, T10 and T12 cages.

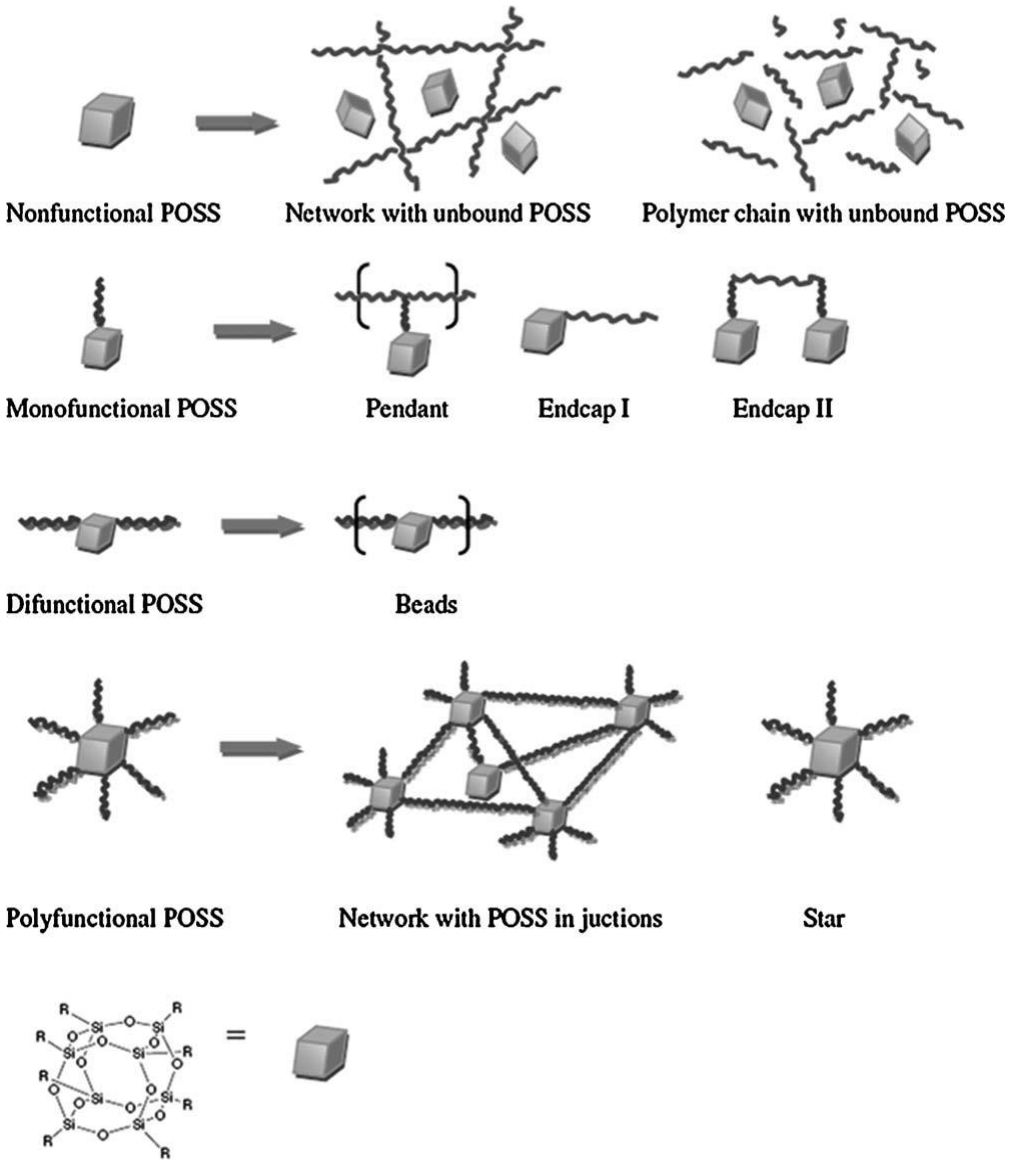

Figure 2.11 : Polymer-POSS constructions.

As illustrated in Figure 2.11, there are four kinds of POSS-based polymers:[56] pendant type which has a single functional group can be reacted as a monomer or co-monomer. Bead type which consists of two polymerizable groups is incorporated in the backbone of a polymer. Star type which can be prepared by polymerizing a POSS cage including multifunctional reactive groups to obtain 3-D networks are hard to characterize. Additionally, there is non-functional POSS cage which disperses in polymeric matrix as filler.

Table 2.2 : Typical properties of POSS

Property	Value or typical behavior
Density range	0.9-1.3 g cm^{-3} typical (up to 1.82 g cm^{-3})
Refractive index range	1.40-1.65
Molecular size	1-5 nm
Form	Colorless, odorless, crystalline solids, some waxes and liquids
Polarity	Very low (fluoroalkyl), low (alkyl), phenyl (medium) to polyionic (high)
Chemical and pH stability	Molecular silicas (closed cage) very stable, trisilanos good stability
Thermal stability	250-350 ˚C typical
Safety	All testing performed has shown POSS to be safe
Purity	Standard purity >97%

Chemistry of POSS is definitely a hybrid with a silicon/oxygen cage (inorganic part) and hydrocarbon functional groups (organic parts) attached to edge Si molecules. As shown in Table 2.2, POSS molecules are substantially large and are almost equivalent to most polymer with its own size measurement which is range from 1-5 nanometer scale. That is the reason for the case that POSS reinforces the physical properties of polymers partly that is impossible via blending of polymers with silsesquioxane resin or inorganic particles. Accordingly, producing high performance and lightweight hybrid nanocomposites are easy to obtain by addition of POSS in the mixture. The performance of product was found to be between polymers and ceramics as illustrated in Figure 2.12[57-59].

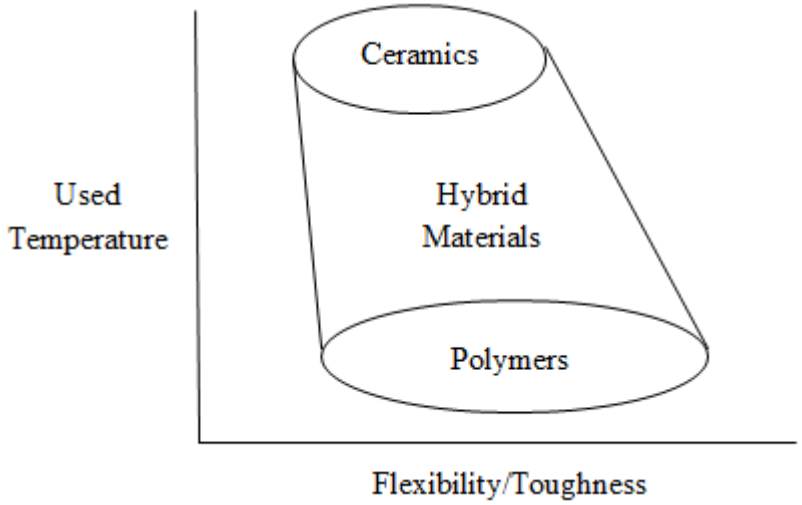

Figure 2.12 : Used temperature versus flexibility/thoughness graphics for ceramics, polymers and hybrid polymers.

POSS-modified polymers have recieved particular attention principally due to their processing simplicity and their exceptional mechanical and thermal properties. Generally, such additives can easily be resolvable in the polymer. When POSS is added to transparent polymers, it is often observed that transparency is maintained up to 5-10 wt% POSS due to solubility of POSS[60]. Otherwise, precipitation appears and cloudiness is detered since additional POSS not any more soluble. POSS solubility is entirely critial to affect on polymer properties. Today, POSS reinforced polymers are also used in film, thin layer, or coating applications. These materials have outstanding dielectric and optical properties. A large number of papers and patents have been affirmed on its usage in interlayer dielectrics, and coating films[60].

As one prominent example for bionanocomposite from plant oils and POSS, Galia et al. prepared the bionanocomposites which contained different amount of POSS with *N*-benzylpyrazinium hexafluoroantimoniate as catalyst. In this study, glycdyl POSS was incorporated into an epoxidized linseed oil cross-linked network, by cationic-initiated polymerization. Enhanced thermal and mechanical properties such as glass transition temperatures and storage moduli were observed. The storage moduli of the networks at the glassy and the rubbey plateau and glasss transition temperatures were observed to be somewhat higher than that of the POSS-free network, due to the reinforcement effect of POSS cages[61].

Ren et al. also studied novel organic-inorganic composites which were prepared by curing hydrogenated carboxylated nitrile rubber with various amount of epoxycyclohexyl POSS at 190 ^{o}C for 20 min under a pressure of 10 MPa. The storage modulus in the rubber region, glass transition temperature, crosslink density and degree of heterogeneity of the composites were found to increase with increasing POSS content. It is also noted that the dielectric constant of the composites decreased with increasing POSS content in the studied frequency range[62].

Serra et al. and reported the effect of the addition of a commercial hydroxyl terminated polyester on the curing process of epoxide/anhydride/amine systems. The increase of hydroxyl groups accelerated the reaction rate at the beginning of the curing but slowed it down at the end. It is found that the best proportion of epoxide/anhydride/hydroxyl terminated polyester cured with tertiary amine which was the stochiometric one. The addition of the hydroxyl groups into the

epoxide/anhydride system slightly increased the global shrinkage. However, the shrinkage after gelation was reduced[63].

In another study, Lu and coworkers reported on the effect of the epoxy-functionalized POSS concentration and curing conditions on the hybrid network properties. As evidenced from the kinetics data, epoxide-functionalized POSS has lower reactivity than N,N,N′,N′-tetraglycidyl-4,4′-diaminodiphenyl methane; hence a pre-mixing reaction was necessary to enhance bonding of the POSS molecules tethers to the networks for improved properties. The glass transition temperature of the networks was found to be strongly dependent on pre-mixing reaction since too short a reaction time caused poor bonding of POSS to the networks while too long a reaction time led to the formation of POSS oligomers that de-homogenized the networks. The SEM studies confirmed that pre-mixing helps to improve the homogeneity of the resins[64].

Addition to these studies, Francos et al. studied that an epoxide-anhydride formulation used for coating materials was modified with a commercially available hyperbranched poly(ester-amide), Hybrane S2200, in order to enhance the thermal degradability of the resulting themoset. They especially examined epoxide-anhydride curing mechanism and the reaction rate of them with and without initiator. They reported that the non-catalysed curing is markedly slower because of the slow reaction of carboxylic acid and epoxide groups. They also concluded that tertiary amines accelerate the curing kinetics of epoxide-carboxylic acid formulations because a carboxylate anionis formed by acid-base proton exchange, which could propagate the reaction in esterification way rather than etherification one[65]. Our research project was aimed to obtain linseed oil modified alkyd resins which have different content of POSS to enhance film and coating features in the light of all these studies.

3. EXPERIMENTAL WORK

3.1 Materials

Refined linseed oil purchased from local markt was used as received. Toluene, acetone, glycerol, calcium hydroxide, phthalic anhydride (PA) (%98) were obtained from Merck and were used as recieved. 1-Methylimidazole (1MI) (%99) was supplied by Sigma Aldrich and Glycidyl POSS (GPOSS) was donated by Hybrid Plastics and both were used without purification.

3.2 Equipments

3.2.1 Fourier transform infrared spectrophotometer (FT-IR)

FT-IR spectra were recorded on a Perkin Elmer FT-IR Spectrum One B spectrometer.

3.2.2 Nuclear magnetic resonance spectroscopy (^{1}H-NMR)

^{1}H-NMR spectra were recorded on an Agilent NMR System VNMRS 500 spectrometer at room temperature in $CDCl_3$ with $Si(CH_3)_4$ as an internal standard.

3.2.3 Thermal gravimetric analysis (TGA)

Exstar SII TG/DTA 6300 was used for TGA analysis. The measurements were done from room temperature to +800 ˚C with a heating rate of 10 ˚C/min. The analysis was used to determine the solid content left when the polymer was heated up to 800 ˚C.

3.2.4 Differential scanning calorimeter (DSC)

The curing temperatures of the samples were determined by a Exstar SII DSC 7020. The samples were first heated from room temperature to 300 ˚C with a heating rate of 10 ˚C/min. The values are reported from the second heating cycle.

3.3 Preparation Methods

3.3.1 Preparation of alkyd resin

Alkyd resin, which was main product of esterification reaction between linseed oil based partial glyceride and phthalic anhydride (PA) was prepared as a comparative sample. In a reactor, the oil and glycerol were heated to 218 ˚C in about 2 hours. Then the lime was added and the temperature was boosted to 232 ˚C to obtain partial glyceride mixture. The temperature was held constant until a clear solution of a sample of the product diluted 1:3 in acetone was acquired. The partial glyceride mixture and amount of phthalic anhydride component which was calculated in pursuant of the formulation as illustrated in Table 3.1[66]. The reaction was carried out at 232 ˚C and maintained for an additional 2 hours.

Table 3.1 : The formulation for preparing a typical simple alkyd resin modified by linseed oil.

Ingredient	Part by Weight (%)
Oil	50
Glycerol	12.5
Lime	0.5
Phthalic anhydride	35
Glycerol	2

3.3.2 Preparation of GPOSS modified alkyd resin hybrid materials

The samples were prepared by thermal curing of a mixture PG and POSS (GPOSS) compounds with anhydride (PA) in the presence of a base catalyst (1MI). The reaction is carried out in toluene medium owing to the solubility of GPOSS[67]. The desired amount of GPOSS (2, 5, 7 and 10 % wt of PG) was dissolved in toluene to increase miscibility of GPOSS in the mixture, and this solution was added to certain preweighted PG mixture into a three-neckled reaction flask. To complete ring-opening reaction, the extra PA (0.5 molar equivalents to the epoxide of theoretical different proportions GPOSS) was added to the mixture. The reaction mixture was homogenized with mechanical stirrer at room temperature for 1 hour. The amount of imidazole catalyst was calculated by 0.0136 mol % relative to PA. After obtaining homogenous mixture, the temperature was increased to 200˚C and the mixture was maintained at this temperature for 2 hours. During the reaction, the esterification

water was produced as by-product, which was removed with toluene. The suggested reaction mixture is presented in Figure 3.1.

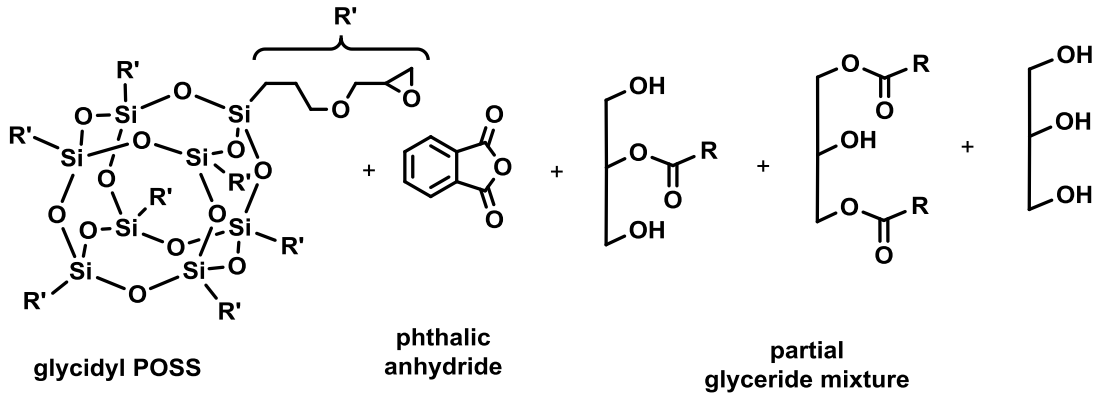

Figure 3.1 : The reaction components of alkyd resin and GPOSS.

3.3.3 Preparation of GPOSS modified alkyd resin hybrid material films

Tolune content of prepared hybrid materials were removed by rotary evaporator. Mixtures, which contained of 40 % wt solid content were prepared. In these mixtures, zirconium naphthenate and cobalt naphthenate were added 0.5 % and 0.05% as metal based on solid content, respectively and all samples were stirred for 10 min. at room temperature. Following this, the film samples applied on a glass plate with a Bird film applicator of 40 μm thickness and were placed in a cabinet at 20 ˚C and 70 % realtive humidity for 24 hours.

3.3.4 Characterization

The structures of GPOSS and alkyd resin and final products were characterized by using Fourier-Transform Infrared Spectroscopy (Perkin-Elmer FT-IR Spectrum One B spectrometer), and Nuclear Magnetic Resonance Spectroscopy (^{1}H-NMR, Bruker 250 MHz, $CDCl_3$ with $Si(CH_3)_4$ as an internal standard). Thermal properties of final products were investigated by a Thermogravimetric Analyser (Exstar SII TG/DTA 6300) and a Differential Scanning Calorimeter (Exstar SII DSC 7020).

Film properties such as flexibility[17], adhesion [18], water resistance [19], alkali resistance[19], acid resistance [19] and drying time[20] were also determined. A Bird film aperature was used for film application. Tin plate panels were employed as a substrate for flexibility and water resistance tests, while glass tubes were used for alkali and acid resistance tests, as explained in the related standart methods.

4. RESULTS AND DISCUSSION

The mechanism of epoxide-anhydride curing is complex due to the both etherification and esterification reactions, which can occur simultaneously. In the absence of amines, an attack of hydroxyl groups on the anhydride molecules forms a monocarboxylic ester (**a**). The monoester then reacts with the epoxide to yield diester containing secondary hydroxyl group (**b**) or protonate an epoxide (**c**), which can homopolymerize by a ring-opening mechanism. The ring-opening polymerization undergo via polyetherification (**d**) by either the active chain end (ACE) mechanism or the activated monomer (AM) mechanism (Figure 4.1)[68].

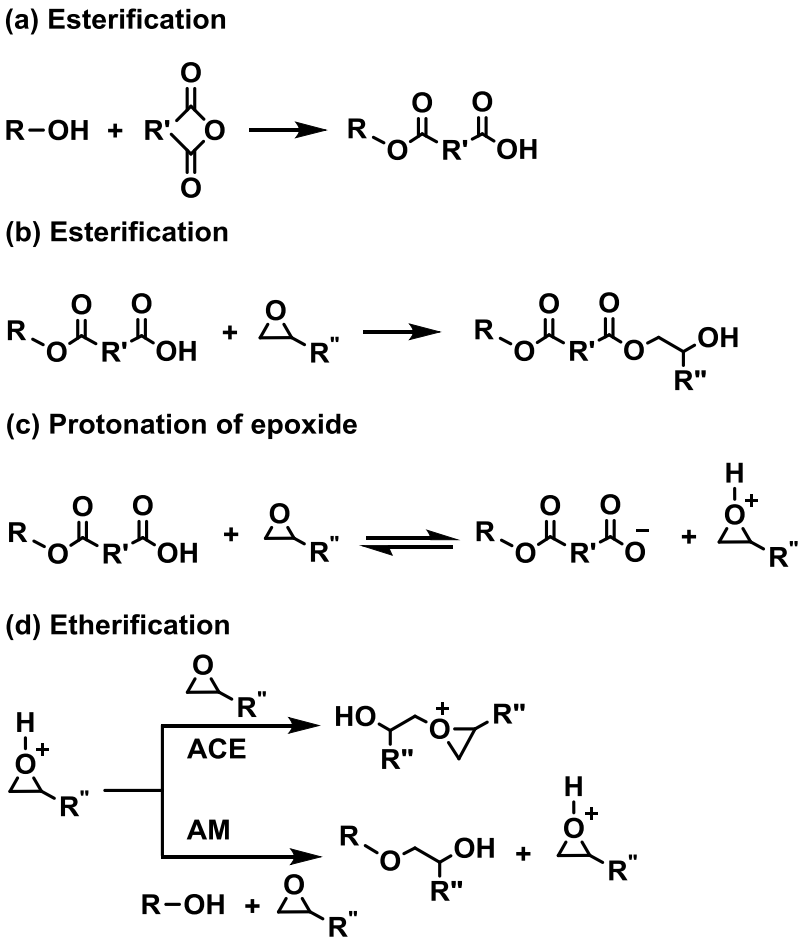

Figure 4.1: The mechanism of uncatalysed epoxy–anhydride formulations

Generally, in industrial production, the strong bases such as tertiary amines, imidazoles or ammonium salts are required to accelerate the curing reaction of epoxy resins with cyclic carboxylic acid and anhydrides. In our case, the use of 1-methylimidazole (1MI) as base catalyst for ring-opening reaction of epoxides overcomes several drawbacks, including long curing time and the high temperature required to acquire optimum properties. The addition of catalyst into epoxy/anhydride curing system drives the reaction mechanism as in Figure 4.2. Initially, the imidazole as a nucleophile attacks to epoxy group of GPOSS to give an alkoxide **(a)**, which is favoured by the presence of proton donors such as hydroxyl groups. This alkoxide anion not only propogate with epoxides via etherification, but also it may preferably reacts with anhydride instead giving rise to carboxylate anion **(b)**. This carboxylate anion would only attack an epoxy group to form another alkoxide. Hydroxyl groups are already present and carboxylic acids are formed in the curing process, and they should be taken into account as acid groups. In order to accelerate the carboxylic acid-epoxy esterification and acid-base equilibrium chain reactions **(c)**, basic catalyst is added. Also, **(d)** and **(e)** show that basic catalyst regeneration reactions, either with alkoxide or a carboylate anion may occur[63].

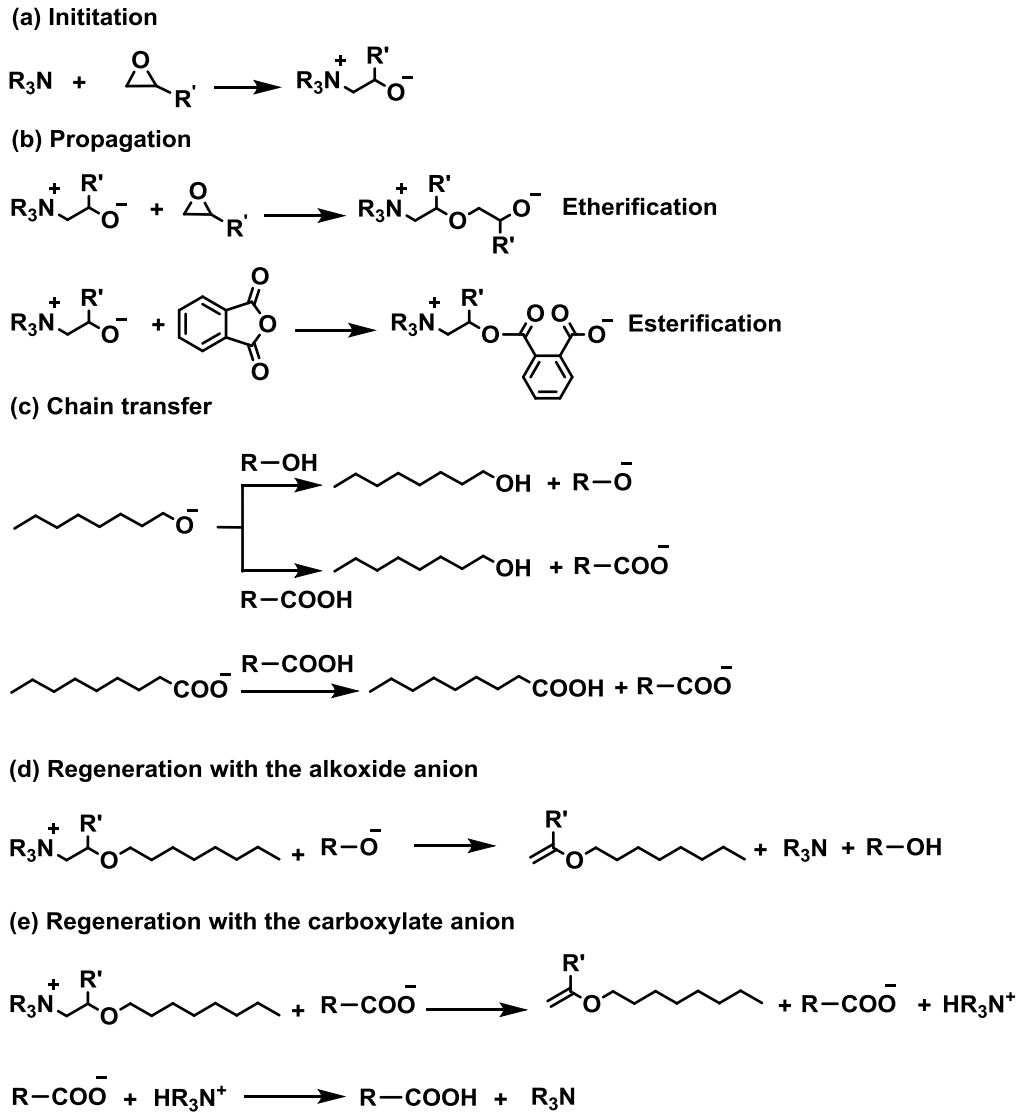

Figure 4.2: Reaction mechanism of the curing of epoxides with anhydrides catalyzed by a basic catalyst.

The purpose of this study is to incorporate polyhedral oligomeric silsesquioxanes (POSS) molecules into alkyd resin structure, which has significantly improved physical and chemical film properties and thermal stabilities of alkyd resins. For this reason, the glycidyl POSS (GPOSS) was inserted into alkyd resin chains by ring-opening and esterification reactions at 200 ^{o}C. As mentioned before, partial glycerides (PG) were firstly synthesized by glycerolysis between triglycerides with glycerol. Then, the GPOSS molecules were combined them through the reactions between −OH group of PG and −COOH group of PA, and −OH group of ring-opened epoxides in GPOSS and other −COOH group of phthalic anhydride (PA) The representative structure of GPOSS modified alkyd resin is shown in Figure 4.3.

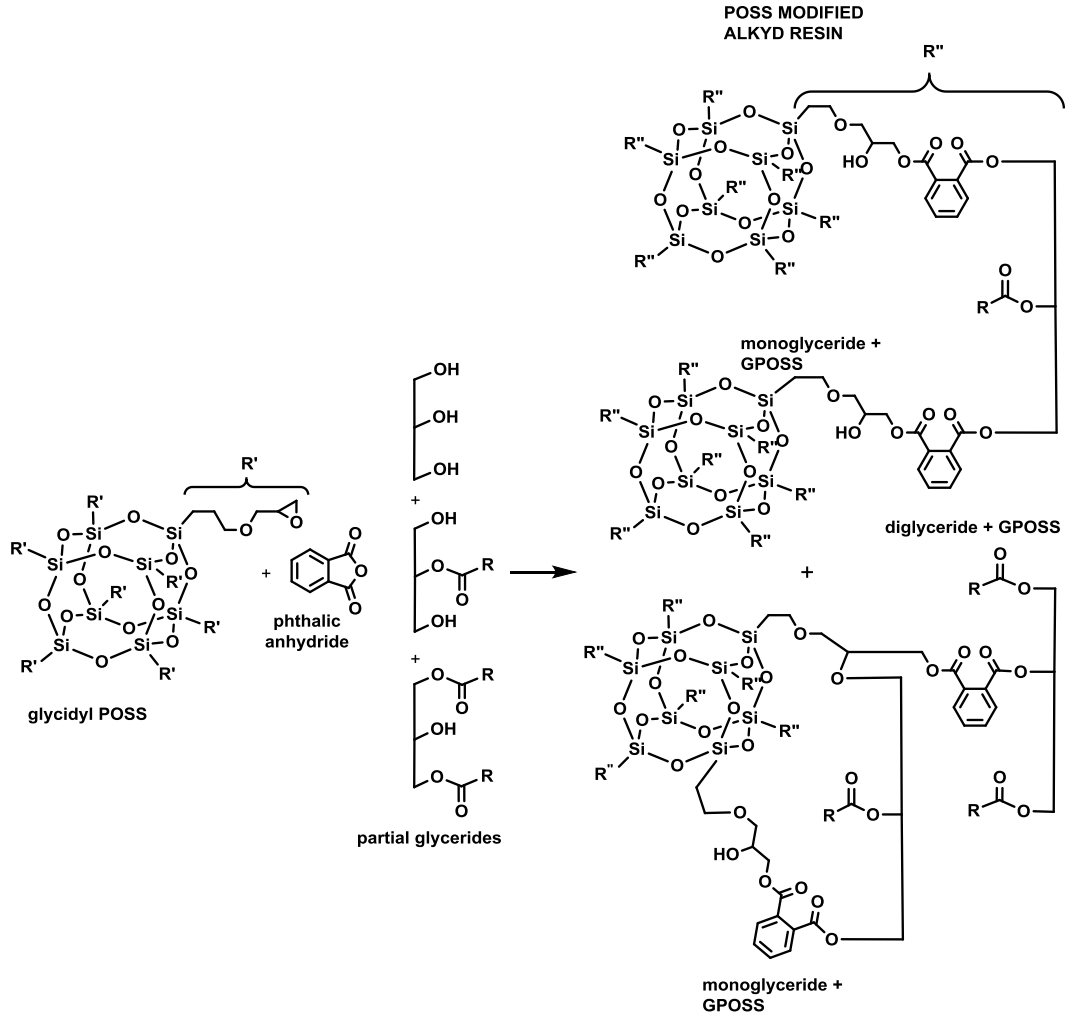

Figure 4.3: Schematic mechanism of PG/ PA/ GPOSS addition reaction.

Our concept is based on the incorporation of GPOSS with linseed oil alkyd resins which provides chemical linking of the diverse molecules. During the study, a series of alkyd resin based hybrid materials (GPOSS modified linseed oil alkyd resins (LA-GPOSS) were successfully prepared by crosslinking between partial glycerides and GPOSS with various concentration (Table 4.1). The curing process was monitored by different characterization methods, such as FT-IR and H^1-NMR spectrometers, TGA and DSC analyses.

Table 4.1: The composition of LA-GPOSS samples with different GPOSS loadings.

Samples	GPOSS (wt%)[a]	Total Formulation			
		Oil (wt%)	Glycerol (wt%)	GPOSS (wt%)	Anhydride (wt%)
LA-GPOSS-2	2	49.3	14.3	1.3	35.1
LA-GPOSS-5	5	48.0	14.0	3.1	35.0
LA-GPOSS-7	7	47.1	13.7	4.3	34.9
LA-GPOSS-10	10	46.0	13.3	6.0	34.8

[a]The weight percentage of GPOSS with partial glycerides.

The influence of catalyst on the curing mechanism was investigated by FT-IR analyses (Figure 4.4). The spectrum of LA-GPOSS without catalyst still contains phthalic anhydride band at 1851 cm^{-1} and epoxide band at 928 cm^{-1} peaks. Since the studied temperature and time are insufficient to complete the esterification reaction between epoxide and anhydride. After addition of 1MI as catalyst, the curing reaction between epoxide and anhydride was completed and the characteristic epoxide and anhydride peaks were not observed. As a result, all curing reactions in these study are required 1MI as accelerator for the ring opening reaction of epoxides and subsequent reactions with anhydride.

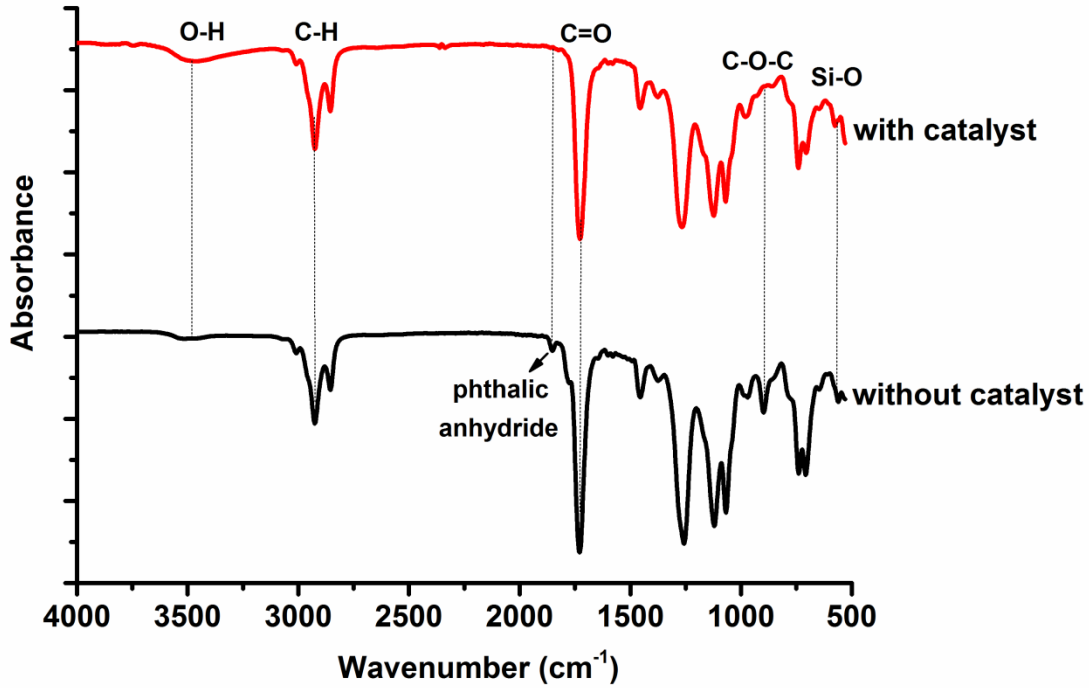

Figure 4.4: FT-IR spectra of LA-GPOSS (a) with catalyst and (b) without catalyst hybrid materials.

The effect of GPOSS concentration onto degree of curing was followed by FT-IR spectroscopy (Figure 4.5). As seen in FT-IR spectra, pure GPOSS has characteristic absorbance peak at 928 cm^{-1} assigned to epoxide ring and at 570 cm^{-1} assigned to Si−O−Si bending. Whereas, pure linseed oil alkyd resin has characteristic ester bond containing C=O band at 1729 cm^{-1} and hydroxyl band at 3493 cm^{-1}. The completion of the ring opening reaction was confirmed by disappearance of epoxide band at 928 cm^{-1}. The consumption of the reactive anhydride was evaluated by measuring the changes in the characteristic carbonyl peak at 1851 cm^{-1}. This group was successfully converted to the aliphatic C=O ester bond due to the esterification reaction between PG, PA and the epoxide groups of GPOSS. After curing of all formulations, not only carbonyl peak of anydride but also epoxide peak of GPOSS were completely disappeared. Moreover, the intensity of Si−O−Si absorption band at 570 cm^{-1} increases gradually with the increase of the concentration of GPOSS, suggessting that POSS nanostructure were chemically incorporated into the alkyd resin. The terminal hydroxyl band produced from oxirane ring opening during the reaction was also observed in the all formulations.

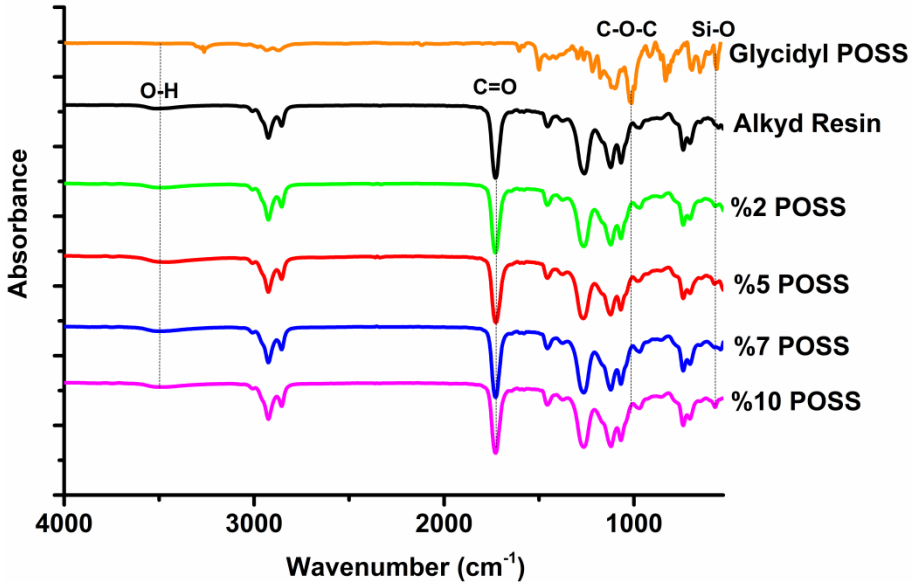

Figure 4.5: IR spectra of (a) pure GPOSS, (b) alkyd resin, (c) LA-GPOSS-2, (d) LA-GPOSS-5, (e) LA- GPOSS-7 and (f) LA-GPOSS-10 hybrid materials.

The introduction of GPOSS into alkyd resin were varified by ^{1}H-NMR as well. In the Figure 4. 6, the characteristic peaks at 2.82 ppm (**f**, O−C**H**$_2$−CH epoxide), 2.60 ppm (**e**, O−CH$_2$−C**H** epoxide) for the epoxide group of GPOSS were determined. After ring opening reactions, these peaks were shifted to 4.30 and 4.41 ppm. Moreover, the

hydroxyl band of ring opened epoxide structure was observed at 5.2-5.7 ppm. The remaining peaks between 0.8 and 2.9 ppm were assigned to aliphatic CH and CH_2 groups of alkyd resins and GPOSS. Furthermore, the aromatic protons of PA were also identified at 7.5 ppm (**h**) 7.78 ppm (**g**).

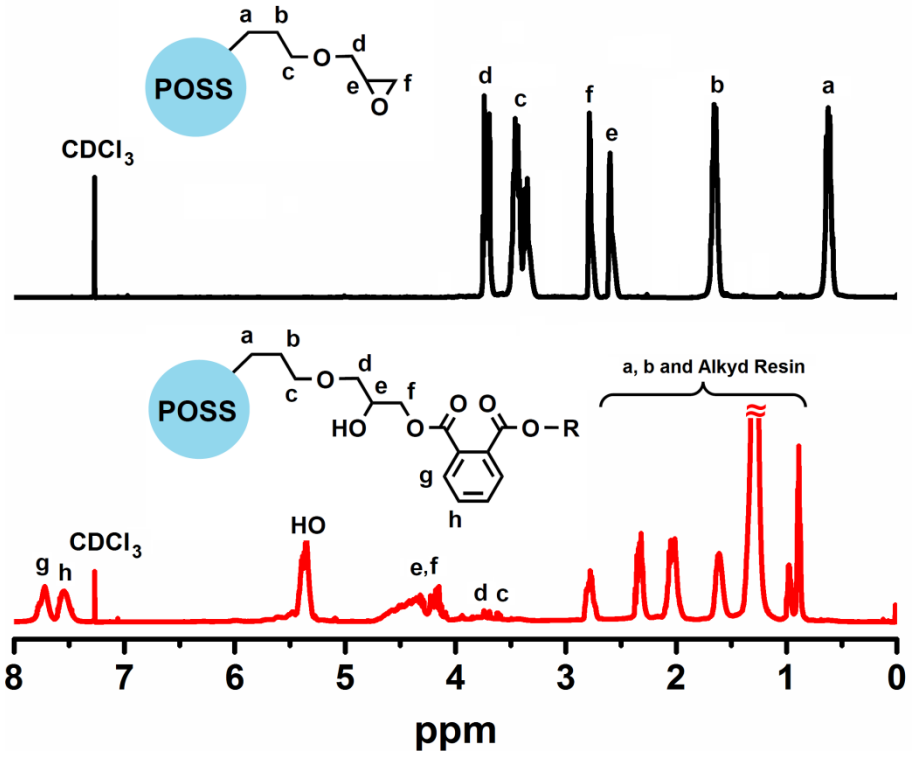

Figure 4.6: ^{1}H-NMR spectrums of GPOSS and hybrid materials.

DSC analysis was used to investigate the influence of epoxide groups of GPOSS in the evolution of the curing process. Figure 4.7 shows the calorimetric curves from 170 to 250 ^{o}C of these mixtures. The neat alkyd resin system showed one exothermic peaks with a maximum at 206 ^{o}C, which could correspond to esterification of hydroxyl groups. In addition, approximate maximum exothermic peaks of LA-GPOSS-2, LA-GPOSS-5, LA-GPOSS-7 and LA-GPOSS-10 were 204, 203, 202 and 200 ^{o}C, respectively. As one can see, there was no much difference in the shape of the exotherm on changing the proportion of GPOSS. Notably, these peaks were slightly decreased with increasing GPOSS concentrations. The increase of GPOSS loadings lead to higher epoxy contents in the system and generated a larger amount of hydroxyl groups after ring-opening reaction. Therefore, the curing temperature needed to reach final apparent degree of cure was the lowest at LA-GPOSS-10. The

addition of GPOSS was very favorable for accelerating the curing process of alkyd resin. This results confirmed that epoxy moiety was key component which can chemically react with PG and PA.

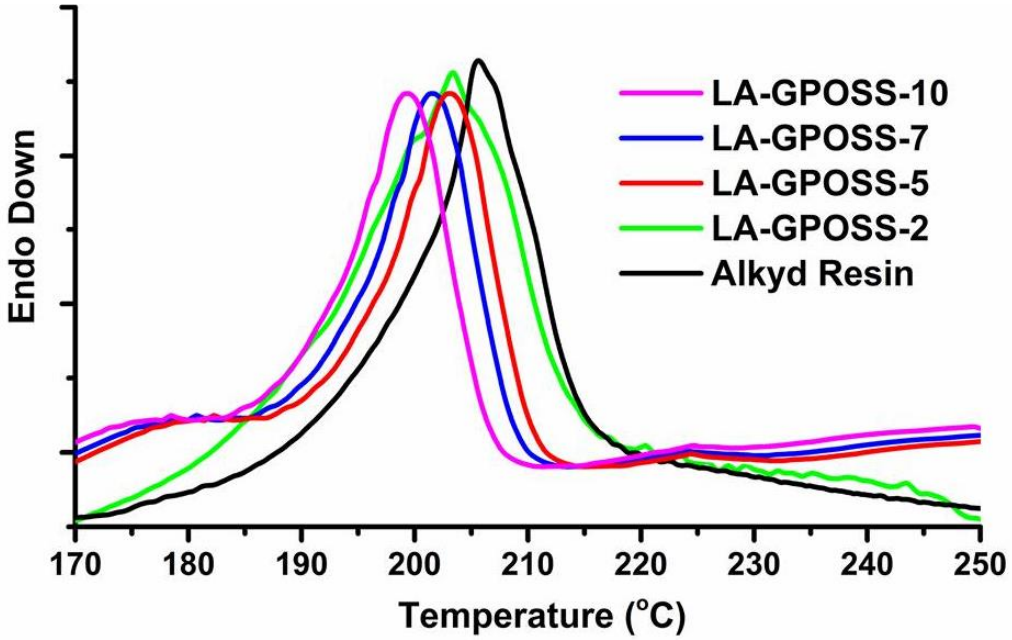

Figure 4.7: Calorimetric curves of neat alkyd resin and LA-GPOSS mixtures.

Thermal properties of cured hybrid materials was investigated by DSC and TGA under nitrogen atmosphere. Since high temperature curing yields highly cross-linked resins, both neat alkyd resin and LA-GPOSS-5 did not have a glass transition temperature, as determined by DSC in nitrogen, propably due to their highly crosslinked nature (Figure 4.8).

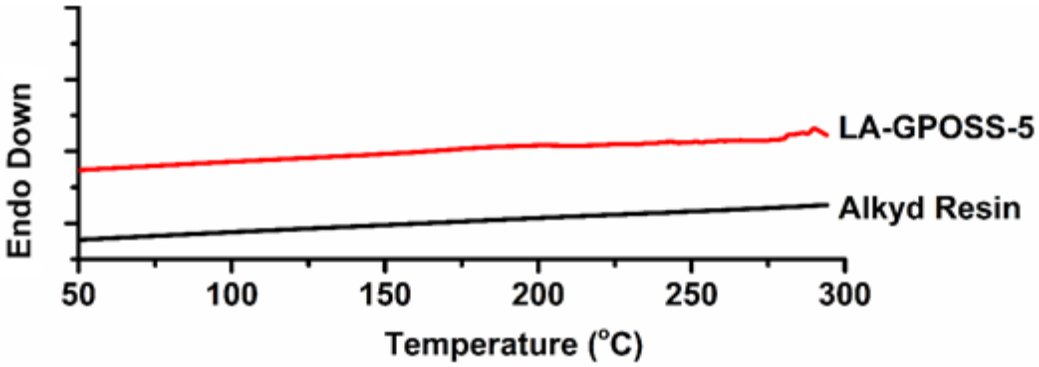

Figure 4.8: DSC traces of neat alkyd resin and LA-GPOSS-5.

The thermal stability of these hybrid materials, defined as the temperature of 10% weight loss, was also measured by TGA. Figure 4.9 shows TGA thermograms of

pure alkyd resin and LA-GPOSS with % 2, 5, 7 and 10 loadings. The temperatures of 10% and 50% weight loss, and the char yield were listed in Table 4.2. For all samples, there is only a single degradation process under nitrogen, which is due to the degradation of the cross-linked polymer network, suggesting that the presence of GPOSS does not significantly alter the degradation mechanism of the alkyd resins. The pure alkyd resin and hybrid networks were degraded approximately at 306-309 ^{o}C. The degradation was resulted from the random degradation of the main chains. The temperature of 50% of weight loss (T_{50}%loss) is significantly increased from 364 ^{o}C to 398 ^{o}C because the POSS cages retard the movement of the molecular chains at high temperature (see Table 4.2).

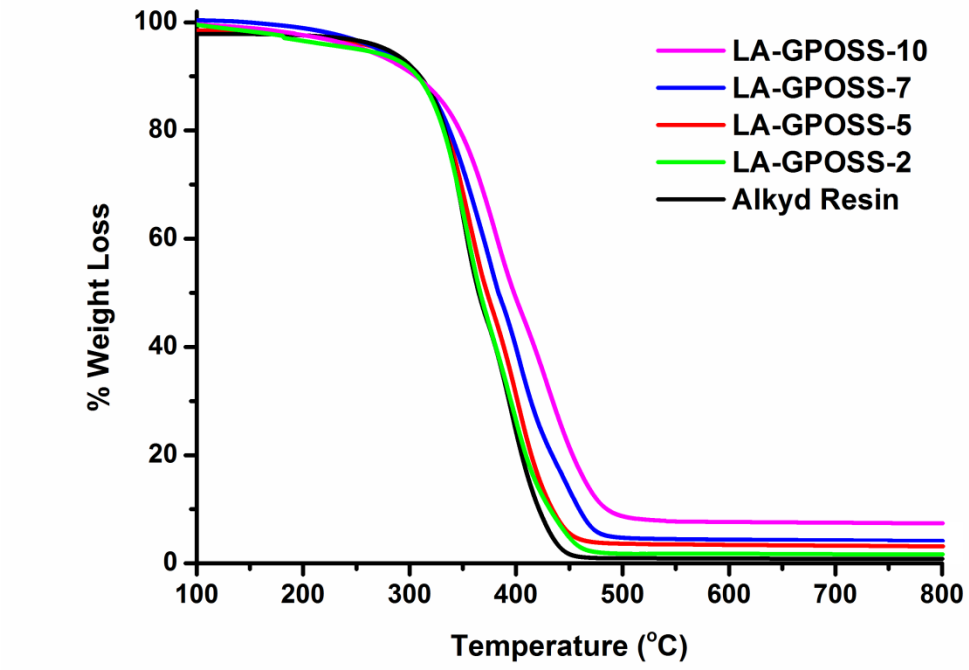

Figure 4.9: TGA thermograms for the neat alkyd resin and LA-GPOSS with % 2, 5, 7 and 10 GPOSS loadings.

The char yield was increased considerably from 1% for pure alkyd resin to 7.8 % for LA-GPOSS-10 at 800 ^{o}C. According the TGA results, decomposition temperatures and char yields of hybrid materials were higher than that of pristine polymer under nitrogen atmosphere. A plausible explanation for these results is that incorporation of inorganic POSS cores not only increase the inorganic content in the networks but also increase the cross-linking densities that hinder the segmental motion of the polymer chains and retarded diffusion of gaseous fragment product. These results

further confirmed that incorporation of uniformly dispersed inorganic GPOSS at molecular level effectively improved the thermal stability of alkyd resins, which provides a good way to enhance the thermal stability of alkyd resins.

Table 4.2: Thermal properties of GPOSS modified hybrid materials.

	Weight Loss Temperature[b]		
Sample	10 wt% (^oC)	50 wt% (^oC)	Char Yield[b] (%)
Alkyd Resin	308	364	<1
LA-GPOSS-2	308	365	1.8
LA-GPOSS-5	309	373	3.6
LA-GPOSS-7	308	383	4.4
LA-GPOSS-10	306	398	7.8

[a] Determined by DSC with a heating rate of 10 ^oC min under nitrogen flow
[b] Determined by TGA with a heating rate of 10 ^oC min under nitrogen flow

All film samples were prepared with 0.5 % zirconium napthenate and 0.05 % cobalt naphthenate as metal based on solid content was allowed to dry by oxidative polymerization at 20 ˚C and 70 % relative humidity for 24 hours. After drying, film properties of neat alkyd resin and LA-GPOSS samples were investigated by various test methods including drying, flexibility, adhesion and resistance to water, alkali and acid tests (Table 4.3). The hybrid film samples displayed excellent resistance to water, acid and had no visible effect on the film after 24 h period. Also, alkali resistance of the film samples advanced with increasing amount of GPOSS contribution The alkyd resin and hybrid films showed excellent flexibility, and did not demonstrate any crack even they were bended over the 2 mm-diameter-cylinder. The adhesion of alkyd resin and GPOSS enhanced hybrid films to glass and metal surface were found to be 5B, as seen in Table 4.3. The long linear alkyl segments of fatty acid provide the flexibility in the network. Also, free hydroxyl and carboxyl groups promote the adhesion of molecules to glass and metal surfaces. The drying time of alkyd resin was increased with the increasing amount of the GPOSS additive. However, the hybrid samples with more than %5 GPOSS concentration showed highly rough surface which is not suitable for coating films.

Table 4.3: Film properties of linseed oil modified alkyd resin and GPOSS enhanced hybrid materials

	Applied Test					
Sample	Flexibility[a]	Adhesion[b] on a glass surface	Acid Resistance[c]	Alkali Resistance[d]	Water Resistance	Drying time[e]
Alkyd Resin	2 mm	5B	no change	30 min	no visible affect	8.0 min
LA-GPOSS-2	2 mm	5B	no change	3.5 h	no visible affect	6.3 min
LA-GPOSS-5	2 mm	5B	no change	4.5 h	no visible affect	5.0 min
LA-GPOSS-7 and above[f]	-	-	-	-	-	-

[a]The diameter of cylinder which caused no crack on the film
[b]Test method B was applied.
[c]Test was carried out at 25 ˚C with 9 % H_2SO_4 solution.
[d]Test was carried out at 25 ˚C with 3% NaOH solution.
[e]The set to touch.
[f]high rough formation on the film surface.

5. CONCLUSION

In conclusion, the incorparation of glycidyl POSS (GPOSS) into alkyd resins was successfully achieved by esterification reaction using 1-methylimidazole as catalyst. Fistly, partial glycerides were prepared from linseed oil and glycerol, and then they cured with different proportions of GPOSS in the presence of phthalic anhydride. The curing reactions were carried out at 200 ˚C for 2h. After this period, the characteristic peak of oxirane ring at 928 cm^{-1} and the peak of the stretching C=O band of PA at 1851 cm^{-1} disappeared. The absorbance of the aliphatic C=O ester bonds due to the esterification reaction at 1729 cm^{-1} increased. Moreover, the proton peaks of epoxide ring in the ^{1}H-NMR spectra were shifted to 4.30 and 4.41 ppm. These results confirmed that GPOSS molecules were chemically incorparated to the linseed oil alkyd resins through both ring opening reaction of epoxide/anhydride and esterification reaction of hydroxyl/anhydride. The curing temperature of the resin is slightly decreased with increasing GPOSS concentrations. According to thermal analysis, the decomposition temperatures and char yields of obtained hybrid materials were higher than that of pristine polymer under nitrogen atmosphere. After the curing, the samples contianing lower than %5 GPOSS showed better film properties such as flexibility, adhesion, drying time, resistance to alkali, acid and water.

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